DEPARTMENT OF GLASS AND CERAMICS

EMR SLAG - PHASE II
(66001)

PHASE II -- FINAL REPORT

A STUDY OF THE HIGH TEMPERATURE ELECTRICAL CONDUCTIVITIES OF SILICATE SAMPLES - MOLTEN STATE

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1. INTRODUCTION

The objective of this program is to measure the electrical conductivity of silicates, over the temperature range from 300°C to 1500°C. This temperature range includes regions where the silicates are solid and regions where they are molten. As such, the program was divided into two phases: the first phase involved the measurement of the electrical conductivity in the molten state up to 1500°C; and, the second phase involves the measurement of the electrical conductivity from 300°C to the softening point of the solid phase. This report covers the work carried out in Phase II of the program.

2. METHOD

The electrical conduction mechanism in most glasses is usually ionic. This is particularly true when the glass contains mobile ionic species such as the alkali ions. There may be some electronic contribution to the total electrical conductivity when multivalent transition metal ions are present in the glass. Electronic conduction then occurs in the form of a valence exchange between ions of different valence.

The electrical conductivity (or resistivity) is usually determined from the measurement of the electrical resistance. The conductivity is related to the resistance by a geometric factor depending on the measurement configuration.

$$\frac{1}{\sigma} = \rho = \text{G.F.} \times \text{Resistance}$$

For flat parallel arrangement of electrodes, the geometric factor is

$$\text{G.F.} = \frac{\text{Area}}{\text{Distance}}$$

The electrical resistance determined from measurements of the current and voltage through the system. The current and voltage are related through Ohm's law

$$V = IR$$

This relies on the linearity of the relation between the voltage and the current and the use of essentially infinite sources and sinks of charge carriers for electrodes. Most electrodes do not satisfy this condition and results in the polarization or "charging-up" at the electrode-sample interface. As a result, most of the voltage drop is across this polarization region and the simple application of Ohm's law is not valid.

Measurements using direct current cannot avoid this problem since the polarization region will grow with time leading to time dependent current or voltages. Measurements made using alternating current prevent the growth of the polarization region. However, a two-terminal measurement still includes the impedance due to the polarization region.

If the resistance of the sample is large compared to those of the electrodes, measurements by two-terminal technique will essentially give the bulk resistance of the sample. At high resistance, however, the resistivity of the material depends on the frequency of the applied electric field following the Debye relaxation process. In reality, the Debye relaxation is always present. However, when the resistivity is low, the frequency at which the Debye dispersion starts is usually at much higher frequency. Thus, the resistivity measured is still the same as the dc resistivity. Even in the high resistivity materials, there will always exist a low enough frequency at which the measured resistivity is essentially the dc value. The resistivity of materials with Debye-type relaxation will appear as shown in Fig. 1. The dc resistivity can be determined from the curve at which there is no resistivity dispersion.

The ac resistance of the sample was measured using a General Radio 716-C capacitance bridge. This instrument is capable of resistance measurement from 3×10^3 Ω at 100 kHz to 8×10^{11} Ω at 100Hz. Below 3kΩ, the measurement was carried out by a direct method using a Brookdeal SC 9505 two-phase lock-in analyzer. The block diagram of the measurement system is shown in Fig. 2.

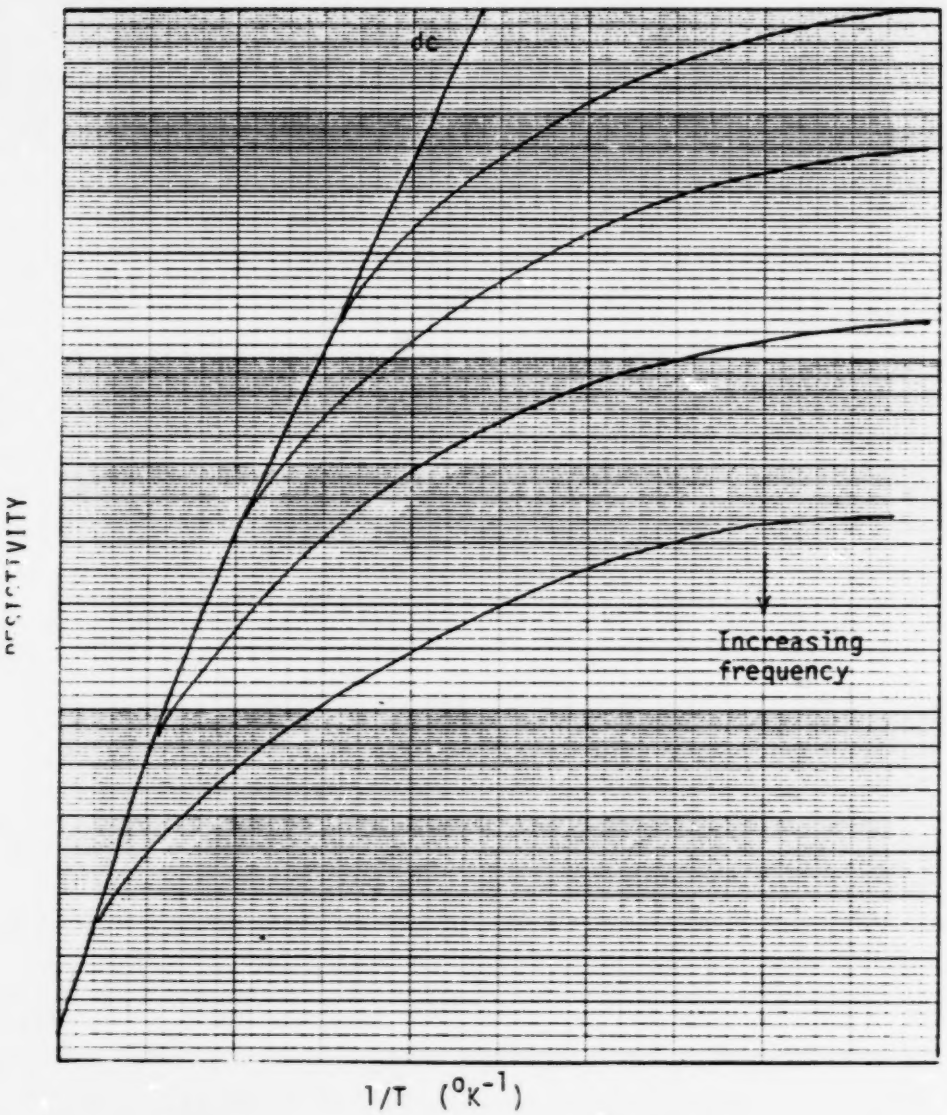

Fig. 1. The expected behaviour of ac and dc resistivity as functions of temperature.

The voltages across the sample and the standard resistor are measured with the frequency being chosen such that both quadrature * components are zero. The current through the sample is obtained from the measurement of the voltage across the standard resistor. This allows the calculation of the resistance of the sample from Ohm's law.

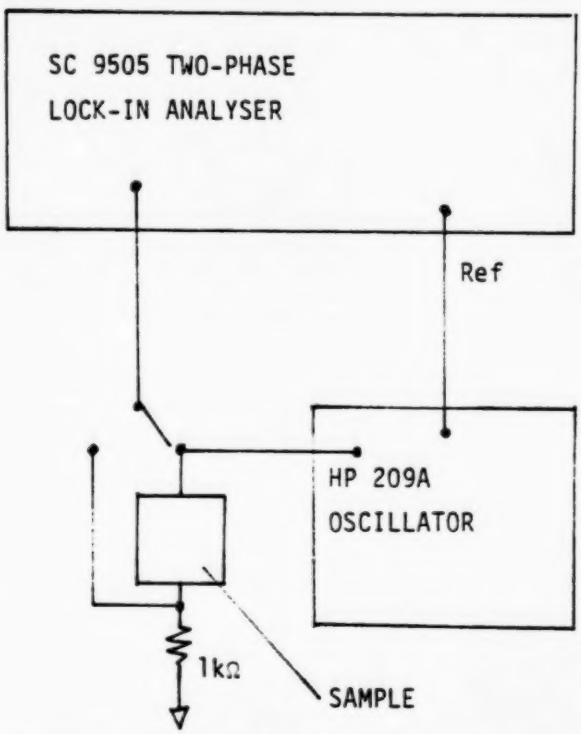

Fig. 2 Block diagram of direct measurement system.

* This was defined in the appendix to the Phase I report.

3. EXPERIMENTAL DATA:

The solid samples specified by the Scientific Authority are the following:

SAMPLE #	COMPOSITION
5	184.5 g basalt #1 + 115.5 g waste limestone
6	300 g basalt #3
7	240 g basalt #3 + 60 g waste limestone
13	243.5 g basalt #1 + 150.5 waste limestone + 4 g soda ash
14	241 basalt #1 + 151 g waste limestone + 8 g soda ash
15	234 g basalt # 1 + 146 g waste limestone + 20g soda ash
16	217 g Nepheline syenite waste + 183 g waste limestone
17	180 g Nepheline syenite waste + 220 g waste limestone
18	240 g Nepheline syenite waste + 160 g waste limestone
24	226 g Nepheline syenite waste + 74g waste limestone

Samples were ground flat to suitable though irregular shapes and polished to 600 grit. The samples could not be saw cut because of residual stress. The residual stress could not be annealed out because the samples crystallized upon heating. It was found, however, that the ground samples were not subject to crystallization.

Platinum contacts were applied on two opposite flat surfaces by dc sputtering. The contacts to the platinum is spring-loaded platinum wire. The yield point of the sample is indicated by the movement of the spring loaded wire. The yield point of the samples are usually at about 750 to 800^{o}C.

The experimental data are shown in the following tables and figures.

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TABLE 1

THE RESISTIVITY DATA FOR SAMPLE #5

E_A = 0.97 ev, ρ_o = 0.485 Ω - cm, A/l = 7.63 cm.

* Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	1.52×10^{10}
	10	1.65×10^{9}
	100	1.56×10^{8}
181	1	9.88×10^{8}
	10	2.39×10^{8}
	100	4.44×10^{7}
275	1	1.46×10^{8}
	10	4.92×10^{7}
	100	9.59×10^{6}
349	1	3.05×10^{7}
	10	1.43×10^{7}
	100	4.92×10^{6}
412	10	5.01×10^{6}
	100	2.16×10^{6}
470	10	1.85×10^{6}
	100	9.89×10^{5}
527	100	4.73×10^{5}
* 586	100	1.94×10^{5}
638	100	9.68×10^{4}
	200	9.38×10^{4}
706	32	4.77×10^{4}
733	35	2.38×10^{4}
768	20	1.91×10^{3}

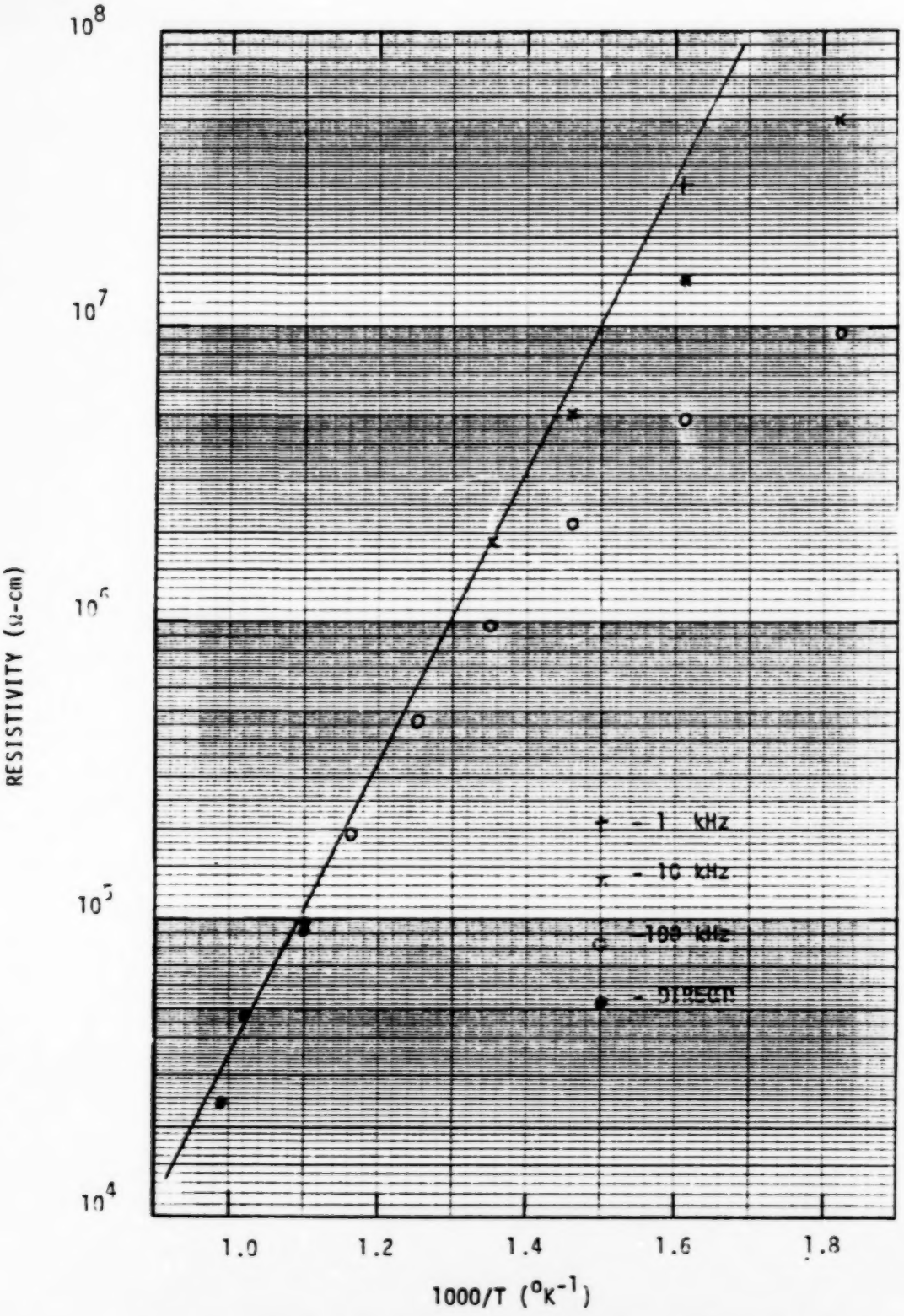

Fig. 3. The ac resistivity of sample #5. The solid line has an activation energy, E_a = 0.97 ev, and an intercept, ρ_o = 0.485 Ω - cm.

TABLE 2

THE RESISTIVITY DATA FOR SAMPLE # 6

E_A = 1.41 ev, $\rho_o = 1.18 \times 10^{-2}$ Ω-cm, A/l = 12.23 cm

* Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	5.54×10^{10}
	10	5.59×10^{9}
	100	5.14×10^{8}
197	1	5.16×10^{9}
	10	5.01×10^{8}
	100	1.50×10^{8}
312	1	5.88×10^{8}
	10	1.74×10^{8}
	100	4.09×10^{7}
397	1	1.38×10^{8}
	10	4.60×10^{7}
	100	1.37×10^{7}
479	1	1.96×10^{9}
	10	1.07×10^{7}
	100	5.04×10^{6}
558	10	3.76×10^{6}
	100	1.89×10^{6}
640	100	6.33×10^{5}
* 716	100	1.47×10^{5}
	200	1.29×10^{5}
762	92	1.05×10^{5}

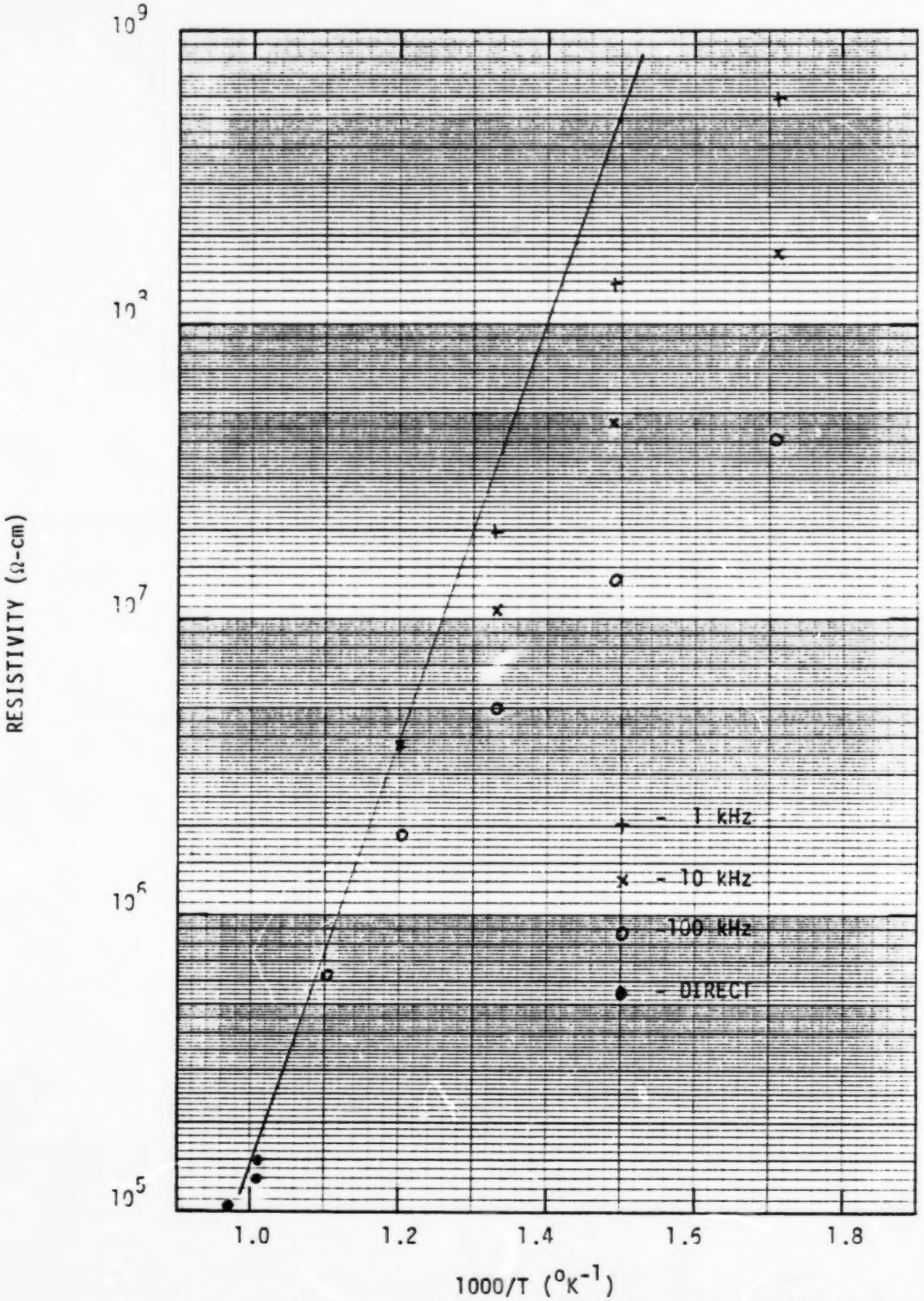

Fig. 4. The ac resistivity of sample #6. The solid line has an activation energy of, E_a = 1.41 ev, and an intercept, ρ_o = 1.18 x 10^{-2} Ω-cm.

TABLE 3

THE RESISTIVITY DATA FOR SAMPLE #7

E_A = 0.98 ρ_o = 1.45 Ω-cm A/l = 6.63 cm.

*Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	4.34×10^{10}
	10	5.23×10^{9}
	100	5.31×10^{8}
195	1	3.90×10^{9}
	10	1.37×10^{9}
	100	1.61×10^{8}
296	1	4.16×10^{8}
	10	1.11×10^{8}
	100	3.13×10^{7}
379	1	4.35×10^{7}
	10	2.65×10^{7}
	100	1.09×10^{7}
478	10	4.92×10^{6}
	100	3.03×10^{6}
551	10	1.58×10^{6}
	100	1.15×10^{6}
631	100	3.38×10^{5}
702	100	1.62×10^{5}
*695	70	1.46×10^{5}
	100	1.50×10^{5}
	200	1.75×10^{5}
742	86	5.68×10^{4}

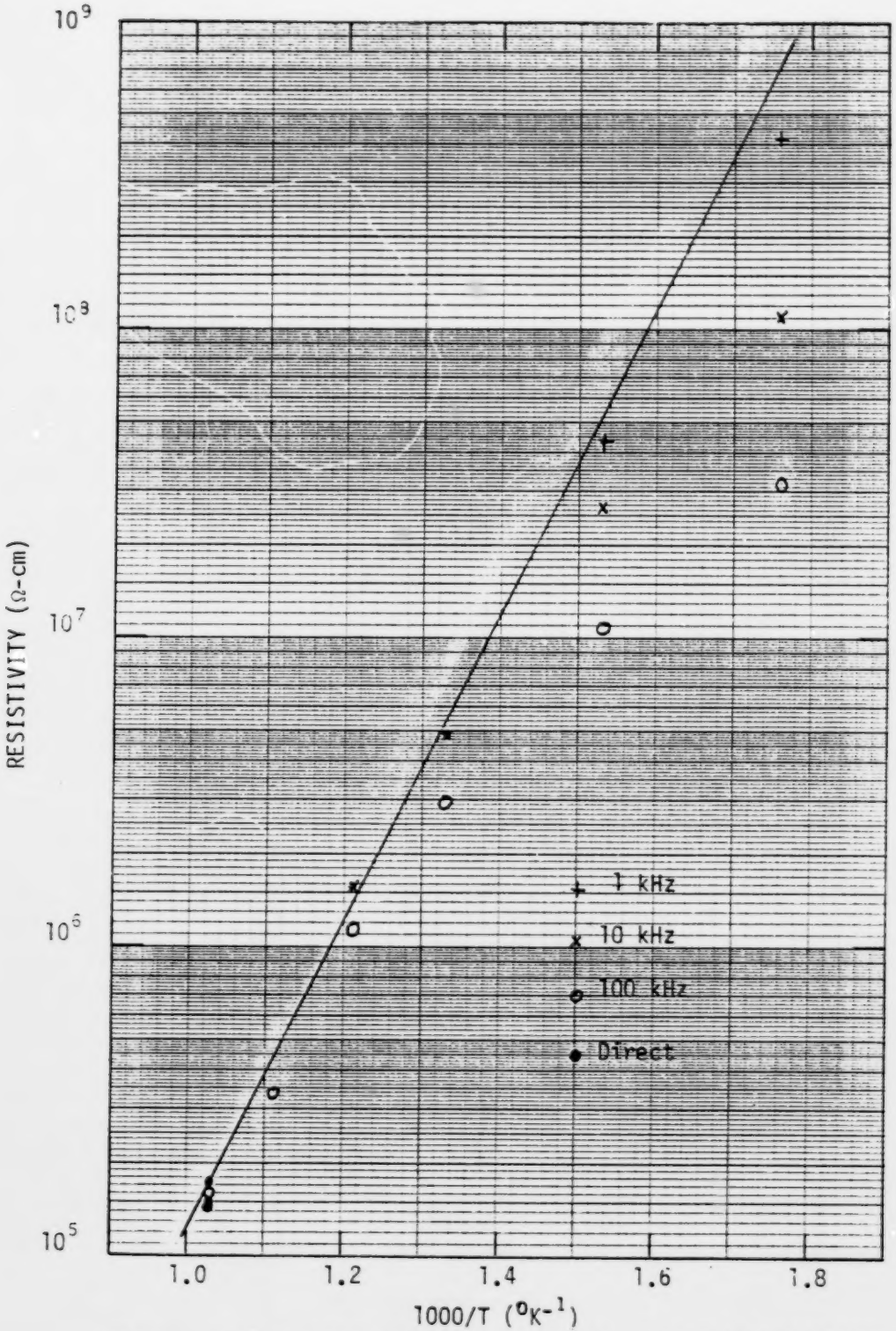

Fig.5. The ac resistivity of sample #7. The solid line has an activation energy, E_A= 0.98 eV, and an intercept, ρ_o = 1.45 Ω-cm.

TABLE 4

THE RESISTIVITY DATA FOR SAMPLE # 13

E_A = 1.19 ρ_o = 0.126 A/l = 8.88 cm.

*Direct Measurement Starts.

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	1.04×10^{10}
	10	3.65×10^{9}
	100	4.47×10^{8}
189	1	4.48×10^{9}
	10	1.01×10^{9}
	100	1.54×10^{8}
266	1	9.09×10^{8}
	10	2.60×10^{8}
	100	5.78×10^{7}
340	1	1.98×10^{8}
	10	7.75×10^{7}
	100	1.36×10^{7}
400	1	5.87×10^{7}
	10	2.69×10^{7}
	100	9.48×10^{6}
459	1	1.96×10^{7}
	10	1.11×10^{7}
	100	4.69×10^{6}
506	10	5.56×10^{6}
	100	2.66×10^{6}
551	10	2.89×10^{6}
	100	1.56×10^{6}
600	10	1.61×10^{6}
	100	8.57×10^{5}
640	100	4.62×10^{5}
692	100	1.93×10^{5}
*692	100	1.61×10^{5}
	200	1.68×10^{5}
728	200	1.31×10^{5}
762	88	8.58×10^{4}

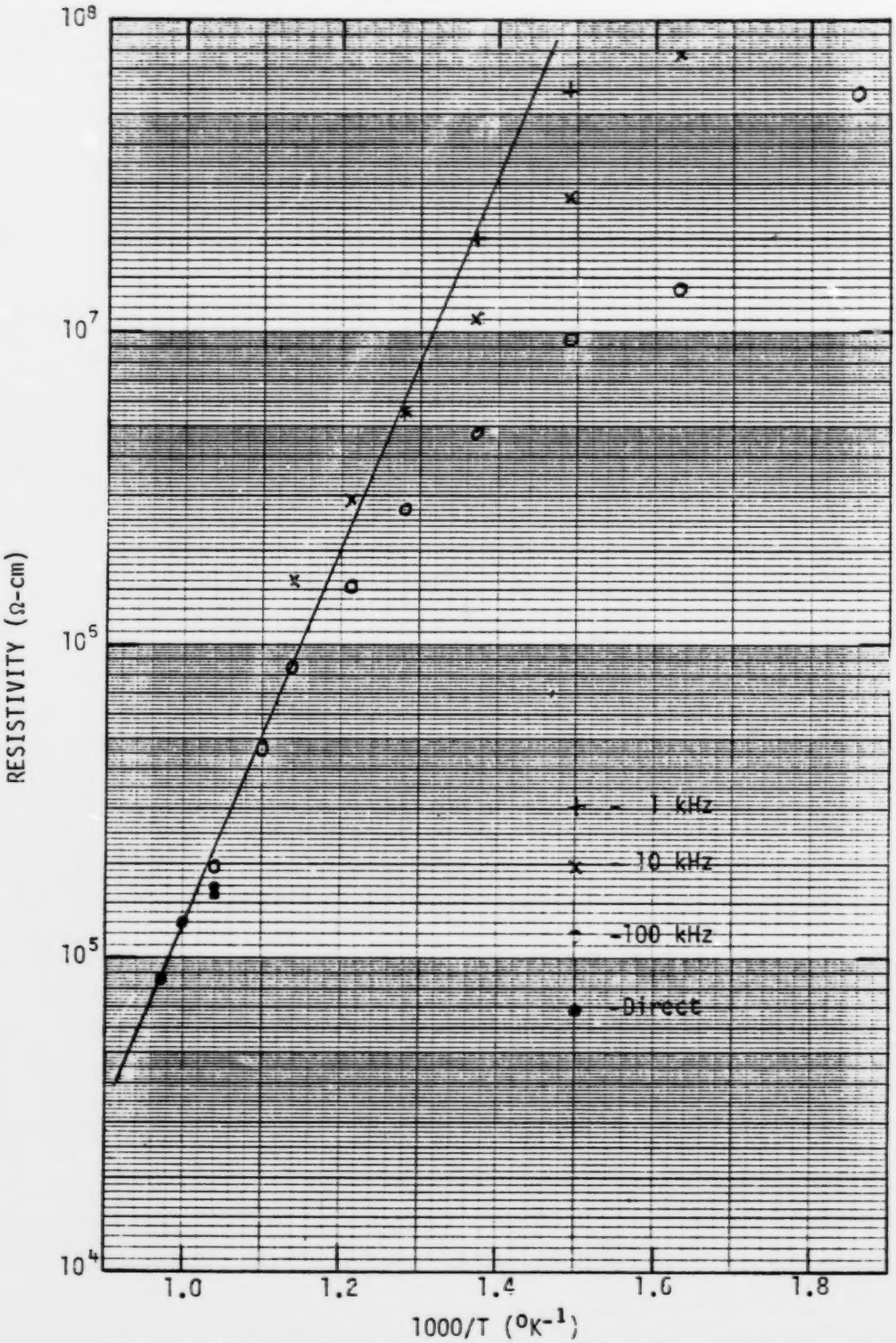

Fig.6. The ac resistivity of sample #13. The solid line has an activation energy, E_A= 1.19 eV, and an intercept, ρ_o = 0.126 Ω-cm.

TABLE 5

THE RESISTIVITY DATA FOR SAMPLE # 14

E_A = 1.31 $\rho_o = 1.88 \times 10^{-2}$ A/l = 4.02 cm.

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	1.07×10^{10}
	10	1.68×10^{9}
	100	2.46×10^{8}
193	1	1.79×10^{9}
	10	4.34×10^{8}
	100	5.95×10^{7}
287	1	3.61×10^{8}
	10	9.89×10^{7}
	100	2.03×10^{7}
356	1	1.07×10^{8}
	10	3.49×10^{7}
	100	9.81×10^{6}
411	1	3.62×10^{7}
	10	1.50×10^{7}
	100	4.54×10^{6}
473	1	1.11×10^{7}
	10	6.01×10^{6}
	100	2.29×10^{6}
527	10	2.59×10^{6}
	100	1.18×10^{6}
591	10	1.11×10^{6}
	100	6.19×10^{5}
631	100	3.49×10^{5}
671	100	1.44×10^{5}
718	100	8.88×10^{4}
*718	100	7.33×10^{4}
	200	8.86×10^{4}
750	150	5.37×10^{4}

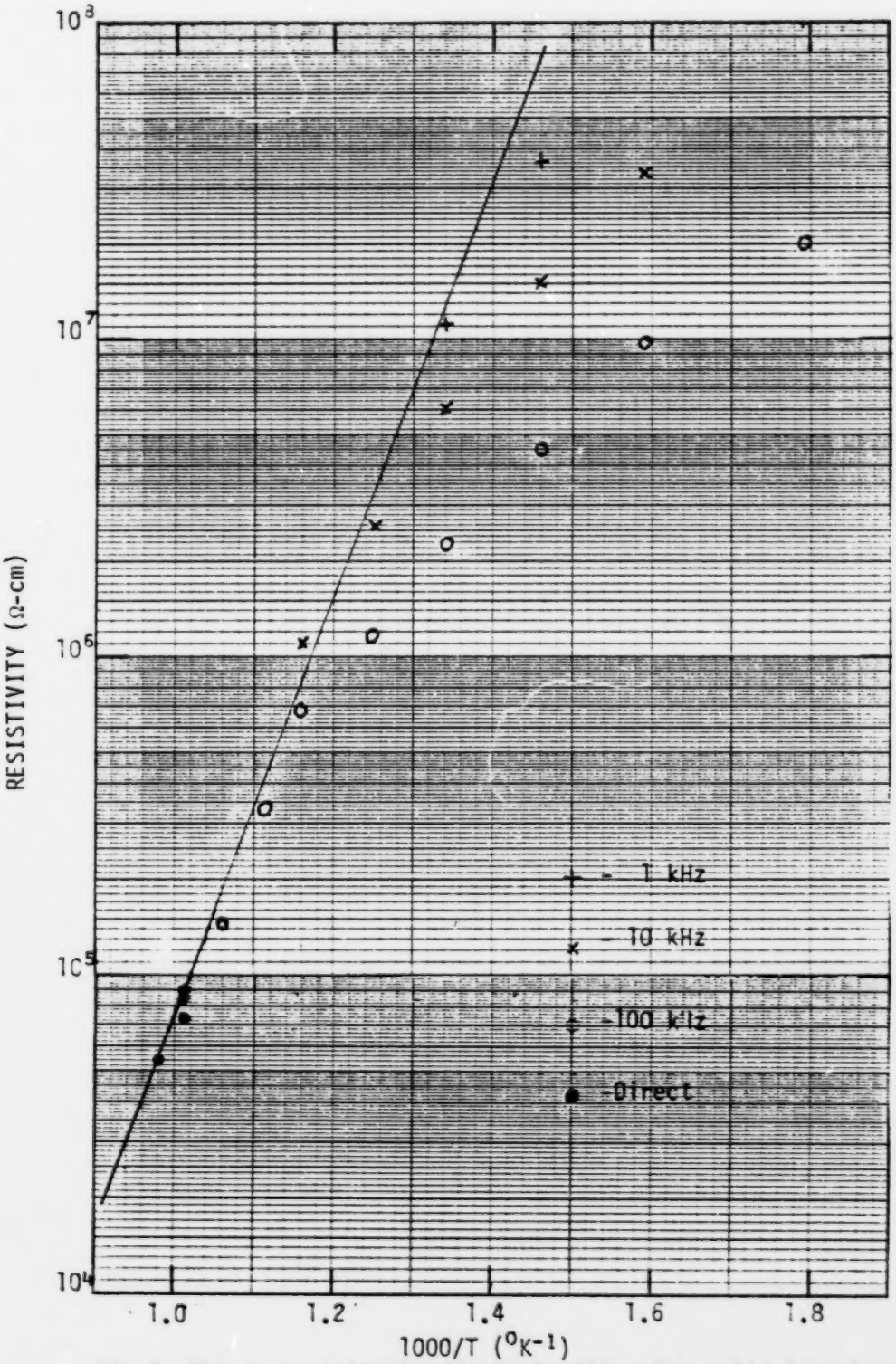

Fig.7. The ac resistivity of sample #14. The solid line has an activation energy, E = 1.31 eV, and an intercept, ρ_o= 1.88 x 10^{-2} Ω-cm.

TABLE 6

THE RESISTIVITY DATA FOR SAMPLE # 15

E_A = 1.40 $\rho_o = 7.59 \times 10^{-4}$ A/l = 7.89 cm.

*Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	5.12×10^{10}
	10	6.69×10^{9}
	100	1.91×10^{8}
137	1	3.72×10^{9}
	10	5.21×10^{8}
	100	1.06×10^{8}
270	1	2.69×10^{8}
	10	8.60×10^{7}
	100	2.30×10^{7}
338	1	5.51×10^{7}
	10	2.45×10^{7}
	100	8.05×10^{6}
382	1	1.34×10^{7}
	10	9.78×10^{6}
	100	4.06×10^{6}
430	10	3.69×10^{6}
	100	1.89×10^{6}
474	10	1.59×10^{6}
	100	9.23×10^{5}
527	100	4.02×10^{5}
571	100	1.99×10^{5}
*572	100	1.79×10^{5}
	200	2.01×10^{5}
614	50	9.80×10^{4}
659	20	3.02×10^{4}
714	30	1.27×10^{4}
738	20	8.84×10^{3}

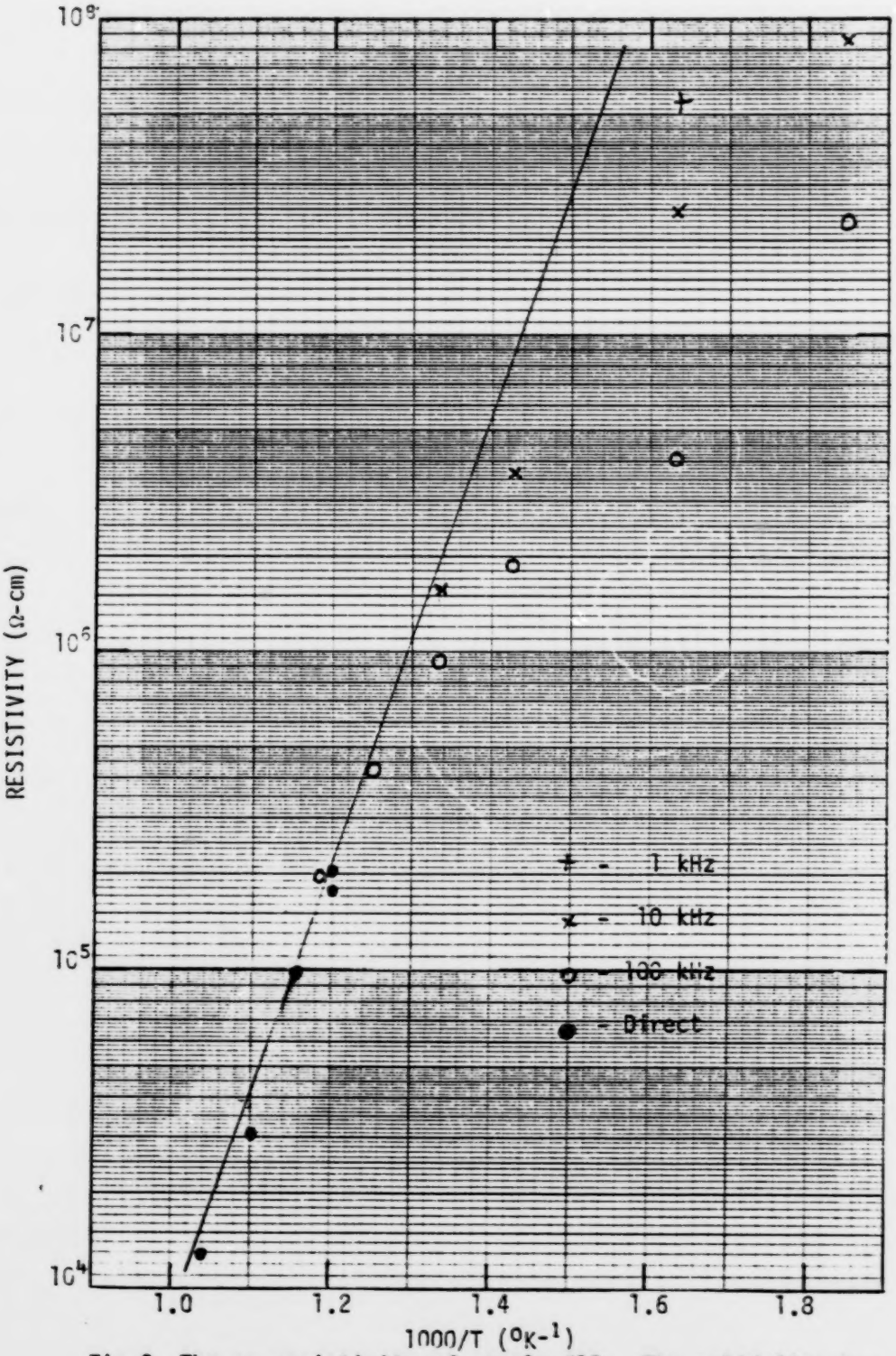

Fig.8. The ac resistivity of sample #15. The solid line has an activation energy, E_A = 1.40 eV, and an intercept, ρ_o = 7.59 x 10^{-4} Ω-cm.

TABLE 7

THE RESISTIVITY DATA FOR SAMPLE # 16

E_A = 1.56 eV $\rho_o = 7.37 \times 10^{-4}$ A/l = 8.91 cm.

TEMPERATURE (^oC)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	2.32×10^{10}
	10	3.21×10^{10}
	100	5.53×10^{8}
174	1	1.43×10^{10}
	10	4.53×10^{9}
	100	3.56×10^{8}
254	1	2.79×10^{9}
	10	6.68×10^{8}
	100	1.22×10^{8}
323	1	6.21×10^{8}
	10	1.93×10^{8}
	100	4.70×10^{7}
247	1	3.35×10^{9}
	10	8.10×10^{8}
	100	1.42×10^{8}
351	1	3.13×10^{8}
	10	1.07×10^{8}
	100	2.81×10^{7}
397	1	1.10×10^{8}
	10	4.73×10^{7}
	100	1.52×10^{7}
432	1	4.72×10^{7}
	10	2.29×10^{7}
	100	8.80×10^{6}
466	1	2.04×10^{7}
	10	1.19×10^{7}
	100	5.08×10^{6}
527	10	3.63×10^{6}
	100	1.98×10^{6}

TABLE 7 (continued)

THE RESISTIVITY DATA FOR SAMPLE #16

E_A = 1.56 eV $\rho_o = 7.37 \times 10^{-4}$ A/l = 8.91 cm.

*Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
558	10	2.13×10^6
	100	1.29×10^6
612	100	5.94×10^5
645	100	2.67×10^5
659	100	1.91×10^5
*659	100	1.64×10^5
699	100	8.91×10^4
726	57	5.44×10^4
754	27	4.15×10^4

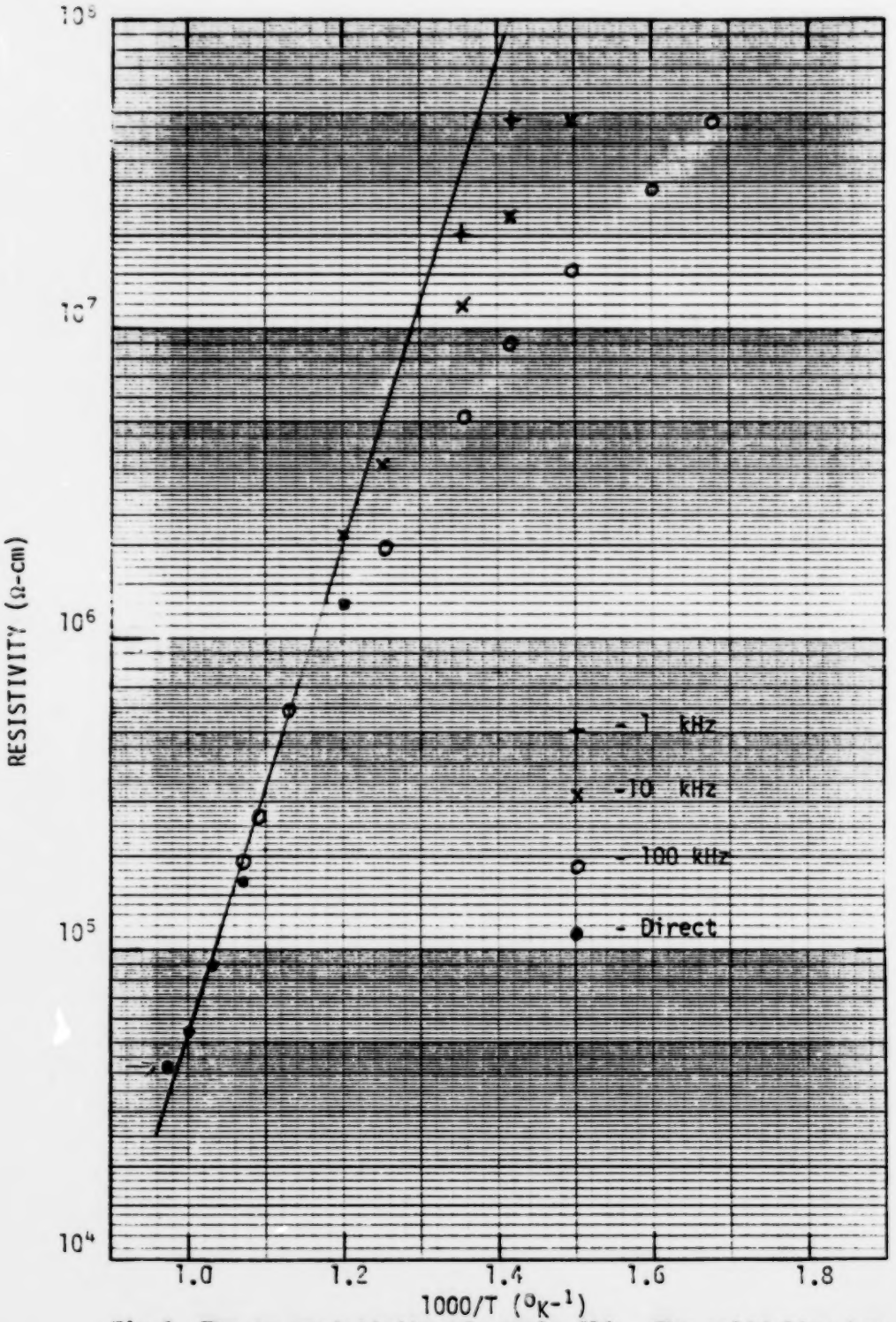

Fig.9. The ac resistivity of sample #16. The solid line has an activation energy, E_A= 1.56 eV, and an intercept, ρ_o = 7.37 x 10^{-4} Ω-cm.

TABLE 8

THE RESISTIVITY DATA FOR SAMPLE #

E_A = 1.20 eV ρ_o = 0.473 Ω-cm A/l = 9.69 cm

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	6.06×10^{10}
	10	5.07×10^{10}
	100	3.38×10^{9}
169	1	2.61×10^{10}
	10	1.30×10^{10}
	100	3.44×10^{8}
279	1	3.41×10^{9}
	10	8.38×10^{8}
	100	1.16×10^{8}
334	1	1.10×10^{9}
	10	3.54×10^{8}
	100	6.67×10^{7}
392	1	2.97×10^{8}
	10	1.30×10^{8}
	100	3.69×10^{7}
447	1	8.42×10^{7}
	10	4.49×10^{7}
	100	1.68×10^{7}
500	1	2.77×10^{7}
	10	1.72×10^{7}
	100	7.68×10^{6}
562	10	7.04×10^{6}
	100	3.35×10^{6}
614	10	2.82×10^{6}
	100	1.63×10^{6}
673	10	1.17×10^{6}
	100	6.26×10^{5}
716	100	2.48×10^{5}

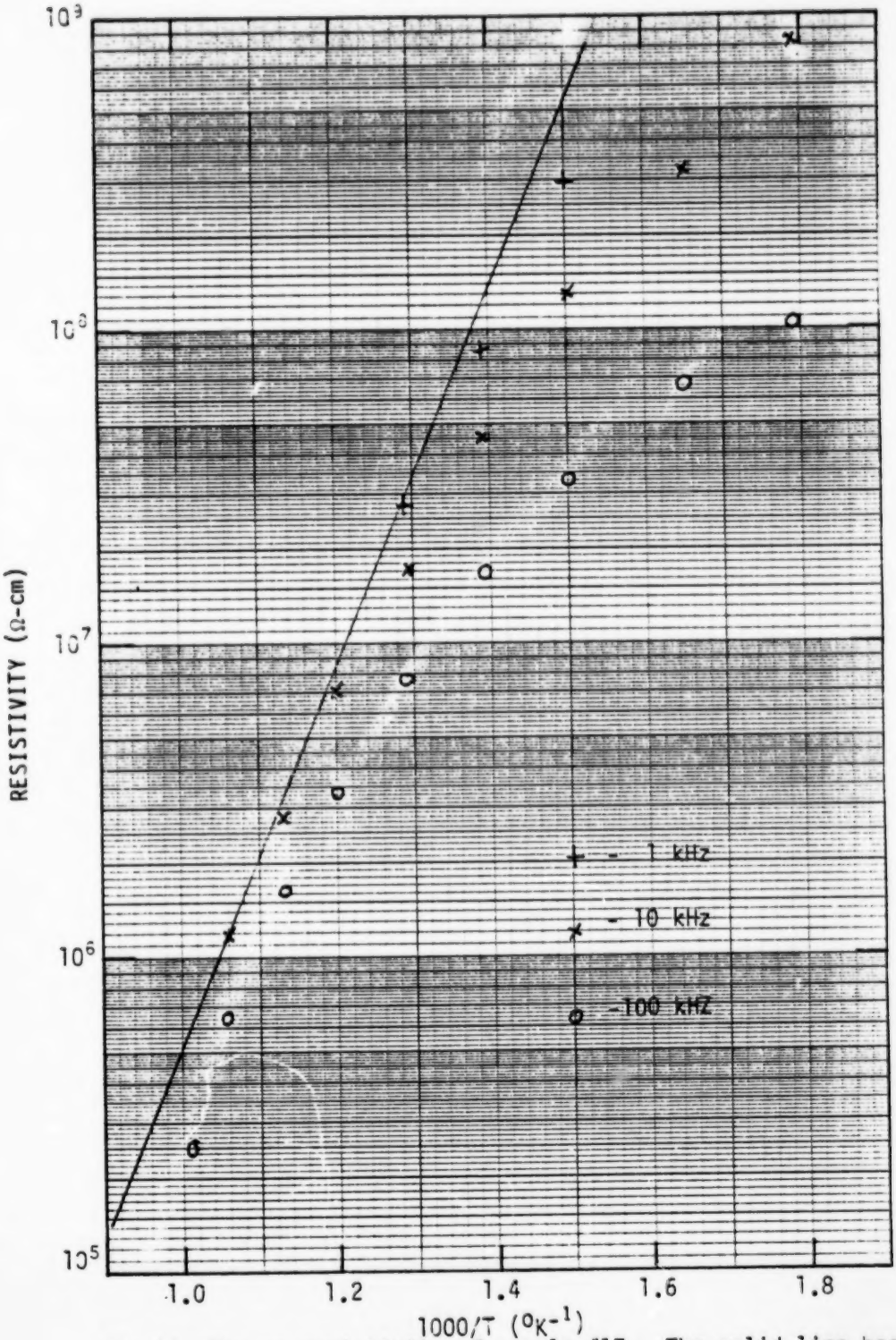

Fig.10. The ac resistivity of sample #17. The solid line has an activation energy, E_A= 1.20 eV, and an intercept, ρ_o= 0.473Ω-cm.

TABLE 9

THE RESISTIVITY DATA FOR SAMPLE #18

E_A = 1.46 ρ_o = 1.48×10^{-3} Ω-cm A/l = 12.4 cm

*Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	5.12×10^{10}
	10	4.43×10^{9}
	100	6.24×10^{8}
213	1	2.94×10^{9}
	10	6.92×10^{8}
	100	1.34×10^{8}
299	1	4.93×10^{8}
	10	1.34×10^{8}
	100	3.69×10^{7}
367	1	9.41×10^{7}
	10	3.88×10^{7}
	100	1.25×10^{7}
422	1	2.57×10^{7}
	10	1.38×10^{7}
	100	5.57×10^{6}
468	10	5.34×10^{6}
	100	2.58×10^{6}
516	10	2.56×10^{6}
	100	1.35×10^{6}
563	100	7.04×10^{5}
612	100	2.94×10^{5}
*652	170	1.09×10^{5}
699	180	5.49×10^{4}
704	140	5.19×10^{4}
745	80	2.58×10^{4}
784	60	1.37×10^{4}

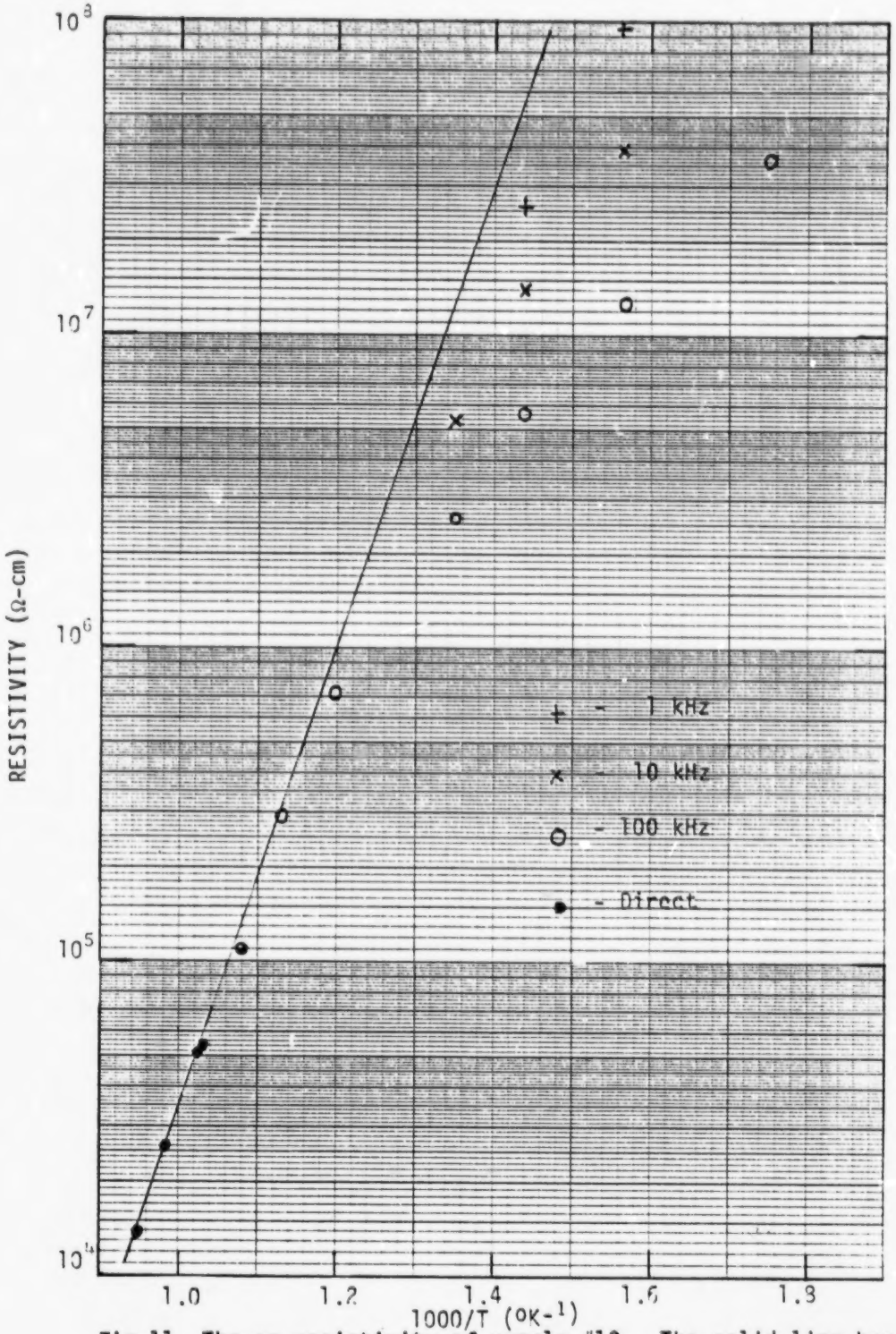

Fig.11. The ac resistivity of sample #18. The solid line has an activation energy, E_A = 1.46 eV, and an intercept, ρ_o = 1.48 x 10^{-3} Ω-cm.

TABLE 10

THE RESISTIVITY DATA FOR SAMPLE #24

E_A = 1.19 $\rho_o = 3.89 \times 10^{-3}$ A/l = 7.85 cm.

*Direct Measurement Starts

TEMPERATURE (°C)	FREQUENCY (kHz)	RESISTIVITY (Ω - cm)
25	1	4.91×10^{11}
	10	5.71×10^{9}
	100	2.05×10^{8}
186	1	8.58×10^{8}
	10	2.48×10^{8}
	100	5.36×10^{7}
258	1	1.22×10^{8}
	10	4.80×10^{7}
	100	1.49×10^{7}
329	1	1.50×10^{7}
	10	8.79×10^{6}
	100	3.98×10^{6}
383	10	2.47×10^{6}
	100	1.49×10^{6}
443	100	4.95×10^{5}
504	100	1.84×10^{5}
*549	65	8.54×10^{4}
600	20	3.47×10^{4}
633	30	1.48×10^{4}
697	20	5.93×10^{3}
731	15	3.44×10^{3}

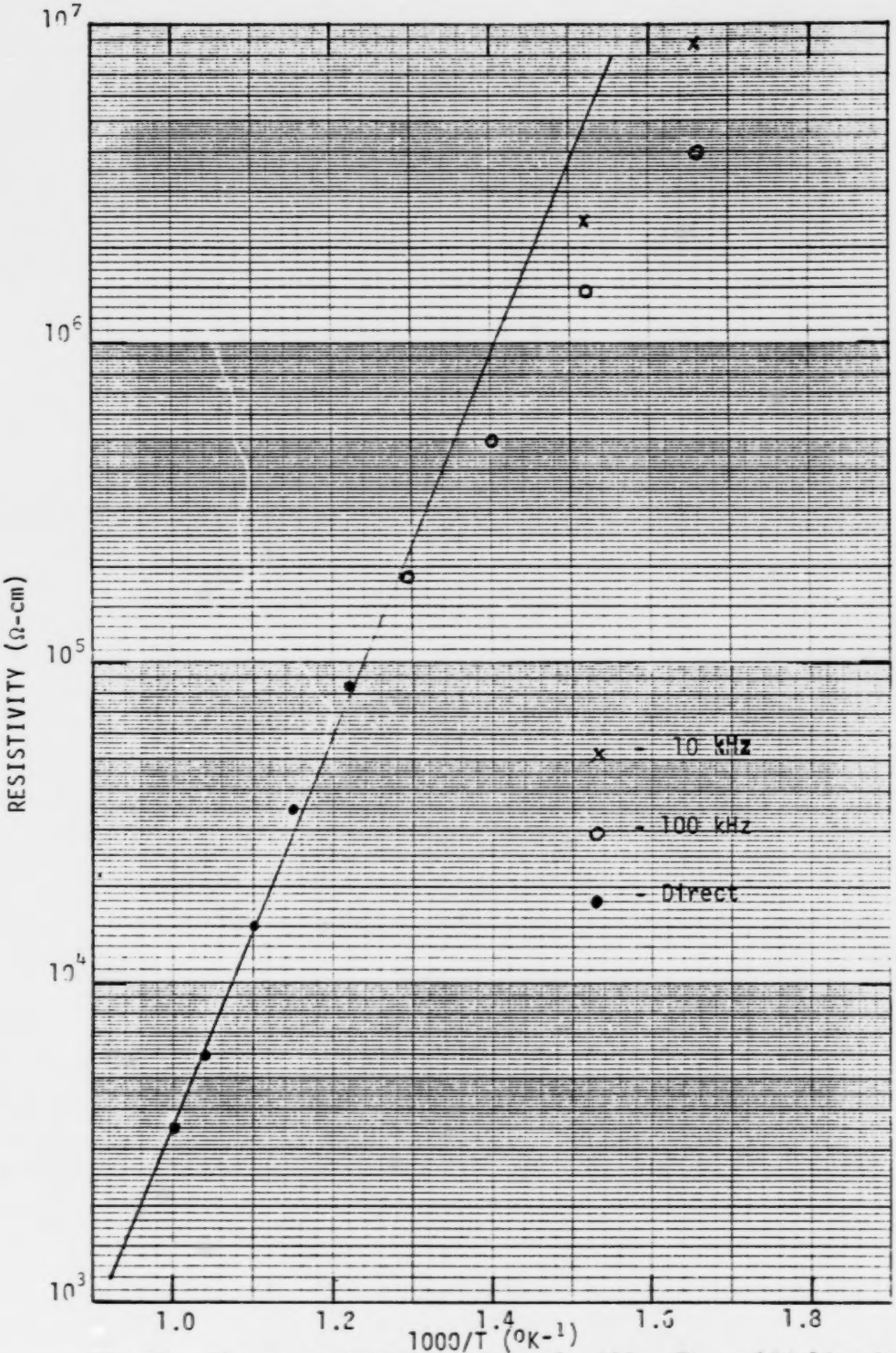

Fig.12. The ac resistivity of sample #24. The solid line has an activation energy, E_A = 1.19 eV, and an intercept, ρ_o = 3.89 X 10^{-3} Ω-cm.

POOR

QUALITY

ORIGINAL